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(54) IMPROVEMENTS IN OR RELATING TO COATED SUBSTRATES

(71) We, INTERNATIONAL PAPER COMPANY, a corporation organized and existing under the laws of the State of New York, United States of America, of 220 East 42nd Street, New York, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an improved process of coating paper and similar materials with polymers and copolymers of olefins. More particularly, it relates to a process of producing polyolefin coated paper having heightened resistance, i.e., improved barrier properties, to the passage of gases such as water vapor and solvents such as fats and oils.

The extrusion of molten polymers and copolymers of the lower olefins, e.g., propylene, ethylene, and butylene, onto a moving paper web is a substantial industry. In the years since development of this industry, the uses for the coated papers have multiplied steadily; so that, today, such varied products as ice cream and dynamite, candy and batteries, frozen foods, liquids of many types, fresh produce, fertilizers, other papers including the photo-sensitive, sugar, bulk chemicals, and animal cages are being contained or lined thereby.

The coating of a polyolefin, such as polyethylene, upon paper is usually accomplished by passing the extruded polyethylene film and the paper simultaneously between two pressure rollers and, thereby, bonding the hot film thoroughly to the paper. One of the pressure rollers is usually rubber-covered and is shielded by the paper web. The other of the pressure rollers, sometimes called the chill roller, is conventionally metal-covered, e.g., chrome-plated, and water-cooled, so as to secure the release of the hot extruded polyethylene film. In this regard, it has heretofore been found that the use, on the premise that their excellent release properties are well-known, of a hot pressure roller having a silicone, a rubber or a polytetrafluoroethylene, for example "Teflon" (Registered Trade Mark) (a commercially available polytetrafluoroethylene) covering in place of the high cooling capacity chrome-plating did not successfully prevent the sticking of the hot extruded polyethylene to such pressure roller and the resultant production-halting breaking of the paper web, because such coverings simply could not stand up to the normal stresses of commercial production. It has also been found that, even at relatively low speeds, the polyethylene film that forms the paper coating must be chilled from extruding temperatures of from 260° to 315° C. to near room temperatures by the chrome-plated roller in a fraction of a second in order to release therefrom. It appeared, therefore, that shock cooling was a requisite of the successful coating of paper with polyolefins. Perhaps for this reason, the industry was unaware of the problem created by this step or tended to ignore it, at least until the issuance of U.S. Pat. No. 3,161,560 on December 15, 1964 and U.S. Pat. No. 3,196,063 on July 20, 1965.

A brief analysis of the nature of polyolefins, using polyethylene as a typical example, is necessary to a proper understanding of what the problem is. Polyethylene molecules are either linear or side-chained and compositions containing them are readily identifiable by their molecular weights, molecular distributions, densities, percentages of chain branchings, and melt indices. Polyethylenes made by low temperature, low pressure catalytic processes tend to contain higher percentages of linear molecules and, because such molecules lend themselves to the growth of compact, dense crystals as the polymers cool and solidify, they are known as linear or high density polyethylenes. Linear polyethylenes are from about 90% to 95% crys-

talline in structure with an amorphous remainder. Polyethylenes made by high pressure, high temperature processes tend to contain higher percentages of side-chained molecules and, because such molecules do not lend themselves to the growth of crystals as the polymers cool and solidify, they are only from about 60% to 70% crystalline with an amorphous remainder. The linearity of the molecules, then, is a factor in the crystallinity and the density of the solids they compose. It is not, however, the sole factor, so that, if it were possible to produce purely linear polyethylene with no molecules having side chains, it would be conceivable that the polymer would pass from being 100% amorphous when melted to being 100% crystalline and having a maximum density of 1.0 when cooled to a solid form. The thermal history of a polyethylene is also relevant and, if such thermal history is unfavorable to the growth of crystals therein, the solid will have a diminished crystallinity and density. It is typical, for instance, for a polyethylene having a high density in the range of 0.945 to 0.950 when supplied to lose such density appreciably, i.e., down to 0.930 to 0.938, when coated on paper by conventional extrusion methods. Polyethylenes of medium density (0.925 to 0.940) and of low density (0.918 to 0.925) show similar, if less dramatic, losses. Hence, it is on account of at least these two factors that all commercially available grades of solid polyethylenes are partly crystalline, partly amorphous mixtures having a density less than 1.0. These densities are expressed in terms of grams per cubic centimeter in accordance with ASTM Test D792-50, Method B, or ASTM Test D1505-57 T, as the case may be.

Practical consequences flow from the mixed character of solid polymers and copolymers of olefins. Where, for instance, a solid polyethylene has a high amorphous content, it has superior gloss, transparency, toughness, and elongation properties. Such properties are desirable in free films, but they have little or no value in captive films, e.g., paper coatings. As paper coatings, polyolefinic films have value almost only when they have good barrier properties, i.e., resistance to the passage of gases such as water vapor and solvents such as fats and oils, these agents being harmful either to the paper itself or to the products wrapped, covered, or contained thereby or, perhaps being desirably prevented from escaping from the packaged goods out through the coated papers. Such barrier properties are, of course, a function of the density of the finished coated papers and, therefore, of the amount of crystallinity of the films coating the papers.

Short of seeking to produce purely linear polyethylene capable of being 100% crystalline in the solid state, then, the most immediate solution to the problem of improving polyolefinic coating films and their barrier properties must be, and has been taken to lie, in the direction of affording the films the thermal history most favorable to crystal growth possible and, throughout their production and application, in maintaining, in preventing any decline in, in restoring any decline in, or even in a heightening of, the amount of crystallinity in any of the polymers and copolymers with which one can coat paper. More particularly, it has been taken to lie in the direction of ascertaining any bad effects on the thermal history of such coating films of their being shock chilled to enable their release from the pressure roller bonding them and, thereafter, overcoming or at least mitigating such effects. So much, then, for the problem giving rise to and the objects satisfied by the present invention.

It has now been found that, in a continuous process of coating a substrate with a film of a polymer or copolymer of a lower olefin, the pressure rollers commonly employed to bond the film to the substrate can still be used, thereby reducing trim losses, bringing greater pressures to bear than an air knife or an electrical field can (in most instances) economically furnish and eliminating the need to retain personnel accustomed to such roller and that shock chilling to obtain film release from one of the pressure rollers can be eliminated, thereby affording the film a thermal history consonant with either an effort to obtain improved barrier properties for smaller amounts of film raw material or an effort to maintain at or improve to a point approaching the theoretical maximum barrier properties of a given amount of film material.

The present invention provides a continuous process of coating a substrate with a film of a compound which is a polymer or a copolymer of an olefin of between 2 and 4 carbon atoms to produce a film-coated substrate of improved barrier properties, which comprises extruding said compound as a film at an elevated temperature, covering a pressure roller prior to carrying out the process with a polyfluorocarbon resin which is extrudable as a sheet when pure, and which has a surface temperature in the range of 200°F to 350°F and forming a bond between said film and said substrate by means of said covered pressure roller. The present invention also provides an apparatus for coating a substrate with a film of a polymer or copolymer of an olefin of between 2 and 4 carbon atoms, which comprises film extrusion means, nip means in proximity of the end of said extrusion means to place the substrate and the film in intimate bonding contact, which comprises a pressure roller previously coated with an extruded sheet of a polyfluorocarbon resin which is extrudable as a sheet when pure, and a backing roller, pressure roller heating

means affording the polyfluorocarbon resin-coated pressure roller a temperature of 200°F —350°F, feed means for the substrate and means for continuously removing the coated substrate.

The term "lower olefin" as used herein indicates an olefin having between 2 and 4 carbon atoms.

More particularly, there is provided an improvement in the apparatus for, and the continuous process of, coating a substrate with a film of a polymer or copolymer of a lower olefin. The improvement resides in operating the pressure roller which impinges against the film in the conventional way at an elevated temperature, i.e., in the range of from 200°F., to 350°F. surface temperature, after the roller has been covered (whether by shrink-fitting as is commercially done by American Durafilm Co., or by shrink-fitting on adhesives as it is commercially done by Pennsylvania Fluorocarbon Company of Fluorodynamics Company, Inc.) with a resinous copolymer of tetrafluoroethylene and hexafluoropropylene which has been prepared generally in accordance with United States Patent No. 2,946,763. In any event, it appears to be the only commercially available polyfluorocarbon resin which can be extruded in its pure form into sheets and tubes, and which, because it contains no fillers or pigments when extruded, has those characteristics needed in the present situation. The pressure roller is coated with this polyfluorocarbon resin before the process of this inverter is carried out.

For a clearer understanding of the invention, reference should be had to the schematic diagram of a process and apparatus embodying the present invention which is contained in the attached figure wherein a substrate designated by the numeral 1, in this case uncoated paper is shown being advanced past pre-heating equipment 2, and into the nip between polyfluorocarbon resin covered, heated pressure roller 3 and a backing roller 4. It also shows a plastics film 5 of a polymer or copolymer of an olefin having between 2 and 4 carbon atoms, coming from the die 6 of a plastics extruder 7 and being advanced into the same nip between the paper substrate and the heated pressure roller. The nip is spaced so as to bring the substrate and the film into intimate, bonding contact.

The attached figure also shows the web of the substrate-film laminate 8 leaving the nip and passing to a cooling roller 9, which is itself water-cooled, before continuing on to the rewinder. It will be understood by those skilled in the art that the distance between the nip and the cooling roller 9 can be increased to allow for a slower cooling of the film on the substrate to give the plastics of the film the most favorable thermal history. It will also be understood that heaters can be introduced between the nip and the cooling roller 9 for the same purpose of achieving a slower cooling. The cooling roller is, of course, ultimately resorted to to bring the temperature of the film down sufficiently to prevent blocking, i.e., sticking, of the plastics at the rewinder.

EXAMPLE

Using high density polyethylene, a substrate of paper moving at approximately 150 to 300 ft./min. was coated with the extruded polyethylene film of various coat weights by operating the "Teflon" FEP fluorocarbon covered pressure roller at an elevated temperature of about 300° F. Then, the coated substrate is allowed to cool from approximately 300° F. to 200° F. by maintaining sufficient web travel before the coated paper contacts a cooling roller. Next, samples of this coated paper were tested for their moisture vapor transfer resistance (MVTR) in a General Goods cabinet in accordance with the recognized testing procedure. Then, the coating weights of previously pressure roller shock-cooled samples of high density polyethylene coated paper having the same MVTR reading in grams of moisture vapor transferred per 100 square inches of sample per 24 hours were compared with the coating weights of the samples made in accordance with the method of the present invention. The results of this comparison are set forth below in Table I wherein Column A shows the coating weight of the polyethylene on paper, in pounds per ream, after extrusion and lamination in accordance with the present invention (and, generally, as depicted in the attached drawing); Column B shows the MVTR reading of the polyethylene on paper, in grams of moisture vapor transferred per 100 square inches of sample per 24 hours, after extrusion and lamination in accordance with the present invention, (generally, as depicted in the attached drawing); Column C shows the coating weight of the polyethylene on paper, in pounds per ream, after extrusion and lamination in a method employing pressure-rolling and shock chilling which gives the same MVTR reading as that shown in Column B; Column D shows the coating weight difference or coating weight saved in pounds of polyethylene per ream of paper between the coating weights of Column A and C giving the MVTR reading in Column B; and, Column E shows the coating weight difference or coating weight saved in percentages between the coating weights of Columns A and C giving the MVTR reading in Column B.

TABLE I

Trial	A Weight Coat Pounds	B MVTR	C Equivalent coat weight for same—MVTR Standard Method	D Coat weight saved—Pounds	E % Saved
1	19.9	0.36	30.2	10.3	32
2	18.0	0.38	28	10.0	36
3	18.0	0.34	30.2	12.2	38
4	19.5	0.36	30.2	10.7	33
5	18.5	0.36	30.2	11.7	36
6	19.7	0.35	30.2	10.5	33
7	12.3	0.68	16.2	3.9	24
8	12.8	0.62	17.8	5.0	28
9	15.2	0.60	18.4	3.2	17
10	12.8	0.69	16.0	3.2	20
AVERAGE %					30

It is to be understood that the apparatus and process of the present invention can be used as described above or in combination with one or more of the systems discussed and depicted in U.S. Pat. No. 3,161,560, issued December 15, 1964; and U.S. Pat. No. 3,196,033, issued July 20, 1965. U.S. Pat. No. 3,161,560 discloses and claims a process of extruding polymers and copolymers of lower olefins as films and forming a bond between the extruded material and a substrate of paper or similar material by blowing a stream of gas against one side of such films. U.S. Pat. No. 3,196,033 discloses and claims a process of extruding polymers and copolymers of lower olefins as films; converging such a film and a substrate of paper, in a selected area; ionizing the air in such selected area; and thereby, subjecting the film to the action of an electric field and forcing it into intimate bonding contact with the substrate. Either of these processes can include a step of heating the film on the substrate, once such film has been bonded to it.

Thus this invention relates to a continuous extrusion coating or laminating process and apparatus wherein a film of a polymer or copolymer of an olefin having between 2 and 4 carbon atoms is extruded and, then, brought into contact with a substrate of paper or a similar material, by means of a pressure roller covered, prior to carrying out the process of the invention, with a fluorocarbon resin which is extrudable as a sheet when pure, and, on the roller, has a surface temperature in the range of 200°F. to 350°F.

WHAT WE CLAIM IS:—

1. A continuous process of coating a substrate with a film of a compound which is a polymer or a copolymer of an olefin of between 2 and 4 carbon atoms to produce a film-coated substrate of improved barrier properties, which comprises extruding said compound as a film at an elevated temperature, covering a pressure roller, prior to carrying out the process, with a polyfluorocarbon resin which is extrudable as a sheet when pure, and which has a surface temperature in the range of 200°F to 350°F and forming a bond between said film and said substrate by means of said covered pressure roller.

2. The process of claim 1 wherein the resin is a copolymer of tetrafluoroethylene and hexafluoropropylene.

3. The process of claim 1 or 2 in which the first and second steps are followed by a third step of heating the film on the substrate.

4. The process according to any one of the preceding claims wherein the substrate is paper.

5. The process according to any one of the preceding claims wherein the film is polyethylene.

6. An apparatus for coating a substrate with a film of a polymer or copolymer of an olefin of between 2 and 4 carbon atoms, which comprises film extrusion means, nip means in proximity of the end of said extrusion means to place the substrate and the film in intimate bonding contact, which comprises a pressure roller previously coated with an extruded sheet of a polyfluorocarbon resin, which is extrudable as a sheet when pure, and a backing roller, pressure roller heating means affording the polyfluorocarbon resin-coated pressure roller a temperature of 200°F—350°F., feed means for the substrate and means for continuously removing the coated substrate.

7. The apparatus of claim 7 which comprises a cooling roller at a predetermined distance to cool said coated substrate.

8. A process for coating a substrate with a film of a polymer or a copolymer of an olefin of between 2 and 4 carbon atoms, substantially as hereinbefore described and as illustrated in the Example.

9. An apparatus for coating a substrate with a film of a polymer or a copolymer of an olefin of between 2 and 4 carbon atoms, substantially as hereinbefore described and as illustrated in the drawing.

10. A coated substrate produced by the process of any one of claims 1 to 5 and 8.

11. A substrate having a film coating when produced using an apparatus as claimed in any one of claims 6, 7 or 9.

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1311968 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*